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Studies on Pollutants. III. Analysis of Uranium at Microgram and Milligram Levels in Waters with *N*-o-Methoxynaphthoyl-*N*-*p*-tolylhydroxylamine

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Abstract

A method is presented for rapid liquid–liquid extraction and simultaneous spectrophotometric determination of U(VI) in the presence of various anions and cations which are usually associated with it in water, rocks, minerals, and fission products using *N*-*o*-methoxynaphthoyl-*N*-*p*-tolylhydroxylamine (MNTHA) in chloroform. The effect of various parameters such as pH, reagent concentration, volume of mother liquor, and foreign ions on the extraction and determination of uranium is discussed. The sensitivity of colorimetric determination of U(VI) with the present method is about 9 times more than the sensitivity of the most sensitive hydroxylamine method reported hitherto.

The method is highly selective as it is possible to accomplish separation of uranium from several anions and cations including those of copper, bismuth, iron, lead, thorium, titanium, zirconium, molybdenum, tungsten, lanthanum, and cerium. The overall process of extraction and determination takes ~20 min. The method is reproducible and has been applied for the analysis of uranium in lake water.

INTRODUCTION

N-Benzoyl-*N*-phenylhydroxylamine (BPHA) (Fig. 1A) and its analogs are versatile complexing agents and have been extensively utilized for separation and determination of a great number of metal ions (*1*). Attempts to find analogs of BPHA, which are more sensitive and selective in their reactions with metal ions than BPHA, have led to the introduction of several substituted hydroxylamines. The first detailed examination of BPHA as a reagent for uranium was carried out recently (*2*). It was found that in the extraction of U(VI), many cations interfered, and the color of the extracted U(VI)–BPHA complex with λ_{max} = 510 nm was suitable only for the determination of milligram quantities of uranium, the molar absorptivity at λ_{max} being as low as 230. The selectivity was also low, and no attempt was made to counter the interference of various common and less common metals which are associated with uranium in minerals and fission products. Subsequently *N*-2-naphthoyl-*N*-phenylhydroxylamine (NPHA) was prepared and tried as a reagent for U(VI) (*3*). NPHA, though proving highly sensitive and selective for V(V) (*4*), came off as only a marginal improvement of BPHA for U(VI) in both sensitivity and selectivity.

N-*o*-Methoxynaphthoyl-*N*-*p*-tolylhydroxylamine (MNTHA) (Fig. 1B) is now presented as a reagent more selective than either BPHA or NPHA and about 9 times more sensitive than NPHA for the extractive colorimetric determination of U(VI). The selectivity of the present method also gives it an edge over the existing colorometric methods (*3*).

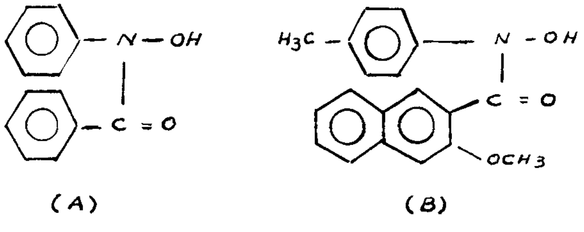

FIG. 1. (A) *N*-Benzoylphenylhydroxylamine. (B) *N*-*o*-methoxynaphthoyl-*N*-*p*-tolylhydroxylamine (MNTHA).

EXPERIMENTAL

Apparatus and Reagents

All chemicals used were of analytical reagent grade unless specified otherwise. Conductivity water was used for all purposes. A stock solution of U(VI) was prepared by dissolving uranyl nitrate in a liter of water and standardizing the solution for uranium (*5*).

MNTHA was freshly prepared from *p*-nitrotoluene and *o*-methoxynapthoic acid by the general method of Gupta and Tandon (*6*). The crude product was recrystallized repeatedly until successive crystallizations gave products of the same melting point, 128°C. The reagent was characterized with the help of microanalysis, IR, UV, and mass spectrometry. It was found to be stable if stored out of contact with light and air. A 0.1 *M* solution of the reagent in ethanol-free double-distilled chloroform was used for extraction work.

The pH measurements were carried out with a digital pH meter (Electronics Corp. of India Ltd.). The absorption spectra were recorded on a Perkin-Elmer model 402 spectrophotometer, and measurements at a constant wavelength were done with an SF-4 (USSR) spectrophotometer. All optical measurements were carried out using matched quartz cells of 10 mm path length.

Extraction Procedure

An aliquot solution of U(VI) containing 12 to 900 μg/ml of uranium was adjusted to pH 4.2 to 4.9 with the help of dilute NaOH or HNO_3 and transferred to a 50-ml separatory funnel. About 4 ml of MNTHA solution in chloroform was added and the phases were equilibrated for about 5 min. After the phases were allowed to separate, the chloroform layer was removed to a test tube containing anhydrous sodium sulfate. The aqueous layer was retained in the separatory funnel and again extracted with a fresh 4 ml portion of MNTHA for 5 min. The extract, after phase separation, was removed and mixed with the first extract, transferred to a 10-ml volumetric flask, and made up to the mark with MNTHA solution. The absorbance of the orange-yellow extract was measured against MNTHA solution as blank. The extracts containing 12 to 80 μg/ml of uranium were measured at 365 nm and those containing 80 to 900 μg/ml of uranium were measured at 525 nm. A calibration curve was set by extraction-colorimetric determination of several known amounts of uranium and by plotting the absorbance (optical density) values against the concentration of uranium. The results were found reproducible within ±0.2%.

RESULTS AND DISCUSSION

Absorption Spectra

The absorption spectra of the uranium extract of MNTHA in chloroform against the reagent (MNTHA solution in chloroform) blank exhibits a sharp peak at 365 nm (Fig. 2) and a broad peak at 512 to 530 nm (Fig. 3). Beer's law is obeyed in the range 12 to 80 μg/ml of U(VI) at 365 nm and 80 to 900 μm/ml of U(VI) at 525 nm; the molar absorptivities are 2100 ±

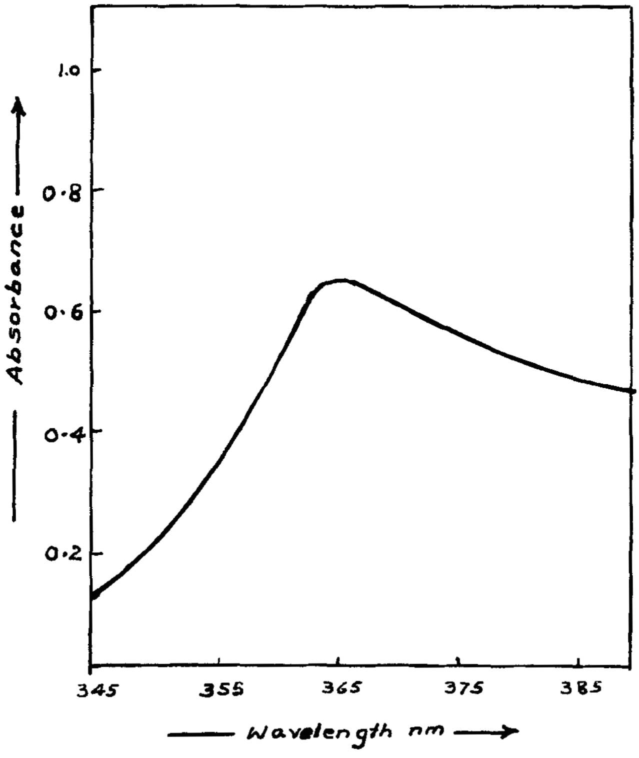

FIG. 2. Absorption spectra of U(VI)–MNTHA system in the near-visible region.

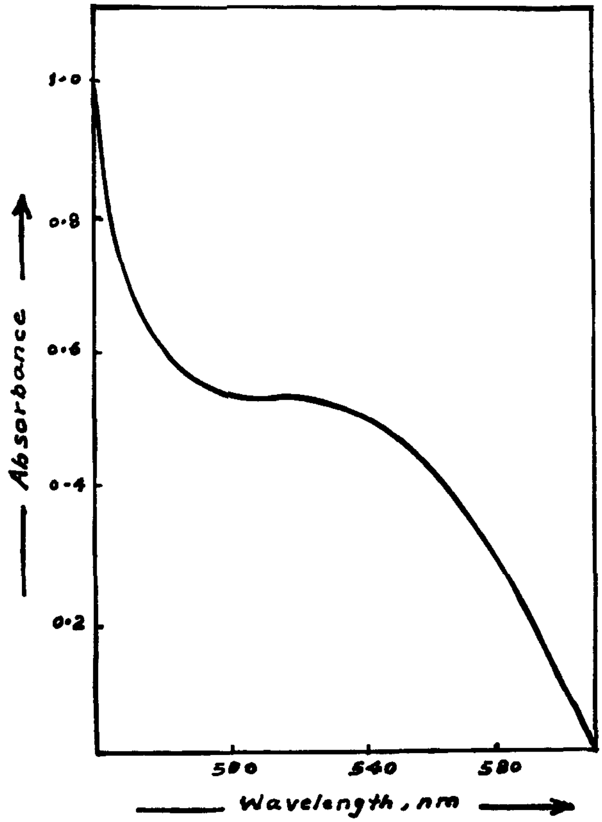

FIG. 3. Absorption spectra of U(VI)–MNTHA system in the visible region.

50 nm at 360 nm and 285 ± 10 nm at 525 nm. Thus uranium, if present in concentrations of less than 90 μg/ml, can be determined using the 365-nm peak while milligram concentrations of uranium can be determined at 525-nm. The sensitivity of the present method, calculated according to the definition of Sandell (*7*), is 0.1 μg/ml of U(VI). This is about 10 times more than the sensitivity of the NPHA method (*3*). Note that the sensitivity for the NPHA method has been incorrectly reported as 0.01 μg/ml. From the absorbance values given in tables, the sensitivity is 1.0 μg/ml. The color of the U–MNTHA complex, as observed by the absorbance measurements of the extracts at various time intervals (1, 4, and 8 hr; 1, 2, 4, 8, and 12 days) was found to be stable for more than 12 days.

Effect of pH on Extraction

Ten milliliter solutions of U(VI) containing 950 μg of the metal were adjusted to different pH values and extracted as described above with 10-ml reagent solutions. It was found that the extraction is quantitative in the 4.2 to 4.9 pH range. Below and above these pH values, the extraction decreases (Fig. 4).

Effect of Reagent Concentration

Extraction of 900 μg of U(VI) was carried out using 10-ml reagent solution, 0.001, 0.01, and 0.1 *M* in MNTHA, the time of equilibration being 5 × 2 min in each case. It was found that extraction was quantitative only

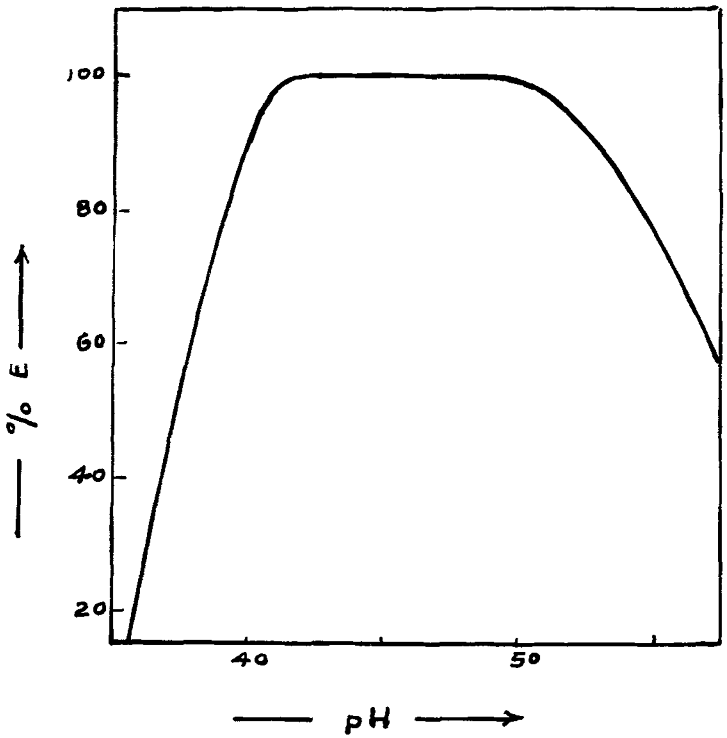

FIG. 4. Effect of pH on the extraction of U(VI) by MNTHA in chloroform.

with 0.1 *M* reagent solutions, the recovery being 50% with the 0.001 *M* MNTHA solution and 85% with the 0.1 *M* MNTHA solution. However, reagent concentrations higher than 0.1 *M* can be used without affecting the accuracy, reproducibility, or extraction time.

Enrichment Studies

Solutions of 5, 25, and 100 ml, each containing 500 μg of U(VI), were extracted with 10 ml of reagent solution as described above. The absorbance values found in all three cases were equal. This shows that a change in the ratio of volumes of chloroform to the aqueous phases from 1 to 20 does not affect the uranium extraction and that the present method can be used to concentrate uranium from its dilute solutions. It also opens up the possibility of using the proposed extraction system for concentrating uranium from its lean sources for large-scale recovery if MNTHA is compatible with such commercial diluents as dodecane and kerosine.

Effect of Foreign Ions

To study the effect of foreign ions on extraction of uranium and to find the concentration limits of foreign ions that are "tolerated" without adversely effecting the extractive-determination of U(VI), different amounts of various ions were added to aliquots of U(VI) solution containing 71.5 μg/ml of uranium. The tolerance limit was set at the amount required to cause ±2.0% error in the uranium recovery. It was observed that the presence of Ca(II), Sr(II), Ba(II), Zn(II), Cd(II), Hg(II), As(III), Ga(III), Gd(IV), Ni(II), Co(II), perchlorate, nitrate, sulfate, and chloride in 10-fold the amount of uranium had no influence. Mg(II), Pb(II), Mn(II), La(III), bromide, iodide, and alkali metal ions are tolerated in the ratio 1:20 or more. Interferences, however, are encountered at all levels from Cu(II), Fe(II), Fe(III), V(V), Ti(IV), Zr(IV), Mo(VI), W(VI), and Bi(III). The tolerance limits are presented in Tables 1 and 2.

Determination of U(VI) in Presence of Bismuth, Thorium, and Cerium(III)

To a solution of uranium containing bismuth, thorium, or Ce(III), a composite solution containing 10 ml of 0.25 *M* EDTA and 5 ml of 0.5 *M* magnesium chloride was added and the extraction of uranium was carried out as described before. This method is efficient for masking bismuth, thorium, and Ce(III) in 1000:1 concentration ratios with uranium.

TABLE 1

Effect of Cations: U(VI) = 71.5 μg/ml, MNTHA = 0.1 *M*, pH = 4.2 to 4.9, λ_{max} = 365 nm

Cation[a]	Added as (μg/10 ml)		Absorbance
None	—		0.635
Ca(II)	$Ca(NO_3)_2$	(9,000)	0.630
Sr(II)	$SrCl_2$	(9,000)	0.635
Ba(II)	$BaCl_2$	(10,000)	0.635
Zn(II)	$ZnCl_2$	(10,000)	0.630
Hg(II)	$HgCl_2$	(8,000)	0.635
Ni(II)	$NiSO_4$	(8,000)	0.635
Co(II)	$CoSO_4$	(8,000)	0.630
Cu(II)[b]	$CuSO_4$	(1,000)	0.632
As(III)	AsF_3	(8,000)	0.635
Mg(II)	$Mg(NO_3)_2$	(16,000)	0.625
Mn(II)	$MnCl_2$	(20,000)	0.628
La(III)	$La(NO_3)_3$	(30,000)	0.625
Ga(III)	GaI_3	(6,000)	0.635
Ge(IV)	$GeCl_4$	(8,000)	0.630
Bi(III)[c]	$Bi(NO_3)_3$	(100,000)	0.630
Th(IV)[c]	$Th(NO_3)_4$	(100,000)	0.635
Ce(III)[c]	$Ce_2(SO_4)_3$	(100,000)	0.632
Pb(II)	$(CH_3COO)_2Pb$	(10,000)	0.628
Alkali metals	Chlorides	(20,000)	0.635

[a] Water of hydration is omitted for brevity.

[b] In presence of CN^-.

[c] In presence of magnesium-EDTA.

TABLE 2

Effect of Anions: U(VI) = 71.5 μg/ml, MNTHA = 0.1 *M*, pH = 4.2 to 4.9, λ_{max} = 365 nm

Anion	Added as (μg/10 ml)		Absorbance
None	—		0.630
ClO_4^-	$NaClO_4$	(10,000)	0.632
NO_3^-	KNO_3	(10,000)	0.630
SO_4^-	K_2SO_4	(9,000)	0.625
Cl^-	KCl	(10,000)	0.630
Br^-	KBr	(16,000)	0.632
I^-	KI	(16,000)	0.635
CH_3COO^-	CH_3COONa	(10,000)	0.630
PO_4^-	Na_2HPO_4	(1,000)	0.628
CN^-	KCN	(2,000)	0.630
EDTA	EDTA-sodium salt	(100,000)	0.630

Separation of Titanium, Zirconium, Molybdenum, Iron, Tungsten, and Vanadium from Uranium

Of these, vanadium, zirconium, molybdenum, and titanium can be removed from solutions containing uranium by prior extraction with 0.1 *M* MNTHA from solutions made, respectively, 20, 4, 2.5, 1, and 0.15 *N* in HCl. Copper can be masked by cyanide and titanium by fluoride.

Iron (di-positive or tri-positive) was removed by prior extraction with 0.1 *M* MNTHA in *n*-butanol at pH 0.9 to 1.2. The results are presented in Tables 1 and 2.

Composition of the U(VI)-MNTHA Complex

Job's method of continuous variation as modified by Vosburgh and Cooper (*8*) was employed to study the composition of the orange-yellow U(VI)–MNTHA complex. The study revealed that U(VI) and MNTHA are combined in a molar ratio of 1:2 in the complex. Potentiometric studies on analogs of U(VI)–N-benzoyl and U(VI)–*N*-nicotinyl hydroxylamine systems had showed that U(VI) is chelated to these ligands as a 1:2 complex at pH$\simeq$4 (*9*). Formation of a 1:2 complex presumably neutralizes the di-positive charges of the uranyl ion and renders the complex hydrophobic and susceptible to extraction in chloroform.

In the present method, the overall extraction and determination takes less than half an hour, and it is possible to extract and determine microgram to milligram amounts of U(VI) in the presence of several ions. Thus the method is rapid, simple, and selective.

Determination of Uranium in Lake Water

In order to test the applicability of the method to polluted waters, uranium was determined in lake water by the standard addition technique. Water samples from the Lower Lake of Bhopal (India) were collected, and varying amounts of uranium(VI) were added to them. The uranium was then determined by the usual procedure. The results (Table 3) indicate the accuracy and precision of the method.

TABLE 3

Analysis of Uranium in the Water of Lower Lake of Bhopal (India)

Uranium added (μg/ml)	Uranium found (μg/ml)	No. of determinations
0.00	0.00	4
0.01	0.01±0.0101	4[a]
0.10	0.10±0.0102	4[a]
1.00	1.00±0.0101	6[a]
5.00	5.00±0.0103	6
10.00	10.00±0.0102	4

[a] Cells with 10 cm path length were used.

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